

while important additional knowledge has been gained, namely, that chloroformed calf vaccine, if originally of sufficiently high potency, will, when prepared and stored under suitable conditions, retain for a considerable time a high degree of potency, and this notwithstanding that the extraneous organisms had been rapidly eliminated from it in an early stage of its preparation.

“Further Experiments on the Production of Helium from Radium.” By Sir WILLIAM RAMSAY, K.C.B., F.R.S., and FREDERICK SODDY, M.A. Received April 14,—Read April 28, 1904.

The research, of which a preliminary account has already been given in the ‘Proceedings,’ vol. 72, pp. 206 and 208, has been continued with the view of ascertaining the volume of emanation produced in a given time from a known weight of radium in the form of bromide, and also the quantity of helium resulting from the spontaneous change of the emanation.

Owing to the minute quantity of material at our disposal, the research has been a somewhat tedious one; but we have succeeded in obtaining fairly concordant measures of the volume of both emanation and helium. The present paper gives a description of the apparatus employed, the methods of experiment, and the quantitative relation between radium and its products.

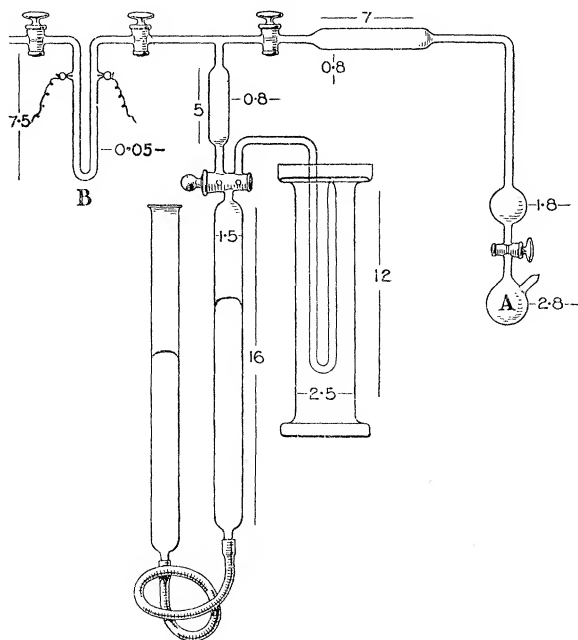
The inactive nature of the emanation from thorium was the subject of an investigation by Rutherford and Soddy.* They concluded “that it is a chemically inert gas analogous in nature to the members of the argon family.” And they continue: “The speculation naturally arises whether the presence of helium in minerals and its invariable association with uranium and thorium may not be connected with their radio-activity.” The discovery was thus the subject of prediction. It followed an attempt to obtain the spectrum of the emanation. Thinking that the spectrum, if brilliant, might be observed by mixing the emanation with a gas of simple spectrum, the first experiments were made by mixing it with helium; but it soon became evident that the helium spectrum overpowered that of the emanation to such an extent as to mask it entirely. And experiments on the removal of gases not belonging to the argon group from the emanation convinced us that its quantity was so small as to require special contrivances in order to deal with it. All apparatus, consequently, was constructed on a minute scale of capillary tubing, less than half a millimetre in

* ‘Phil. Mag.,’ 1902, 6, vol. 4, p. 581.

diameter. Approximate measurements of the scale of the apparatus in centimetres are given in the sketches.

Fig. 1 gives a sketch of the first apparatus, which was soon abandoned; suffice it to say that an attempt was made to accumulate the emanation in A, which contained a solution of several grammes

FIG. 1.



of impure chloride, obtained from very impure carbonate, and to examine its spectrum in the U-tube B, made of capillary tubing, with electrodes of platinum as shown. The spectrum was that of carbon monoxide and dioxide.

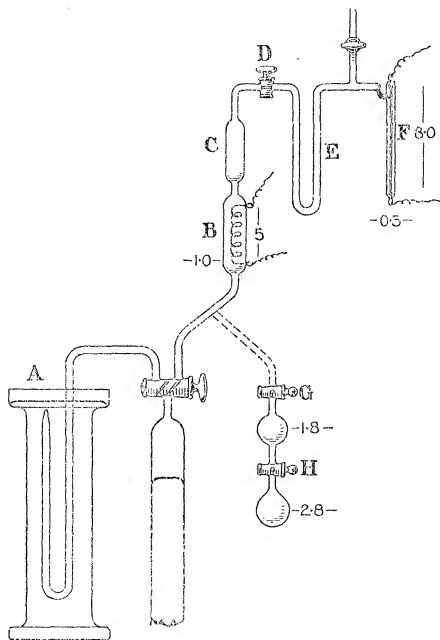
Experiment 1.—A brief description of this experiment has already been given.* Twenty milligrammes of radium bromide was dissolved by admitting water boiled *in vacuo* to the crystals in the bulb A (fig. 1), which had previously been freed from air with the pump. The bromide, as a letter from the seller informed us, had been prepared in the solid state about $2\frac{1}{2}$ months. The evolved electrolytic gas containing the emanation was collected through the pump and introduced into the apparatus, of which a sketch is given in fig. 2. Before this was done, the whole apparatus had been exhausted, and washed out with oxygen several times, admitted through the gas-

* *Loc. cit.*, p. 206.

burette. The emanation, too, was collected in a tube which had been used for oxygen, the object being to keep nitrogen out of the tubes, and so to avoid its spectrum, which is difficult to remove.

The gas, of which there was about half a cubic centimetre, was admitted into the gas-burette through the inverted siphon A; the stop-cock being reversed, it was passed slowly into the tube B, which contained a spiral of thin, partially oxidised copper wire, and which had previously been exhausted; during the introduction of the gas the copper spiral was kept red-hot by a current. The water produced was

FIG. 2.

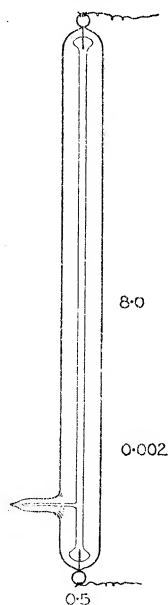


absorbed in the tube C, which contained phosphorus pentoxide. Mercury was then admitted into B and C, so as to displace the gas through the stop-cock D, which was then shut. The vacuum tube F had been previously glowed out until phosphorescent. This vacuum tube is represented in natural size in fig. 3; its capacity was about one-third of that of the U-tube and accessory tubing. The spectrum of carbon dioxide was alone seen. With a jar and spark-gap interposed, on comparing the spectrum with the jar discharge in a similar tube containing carbon dioxide, a yellow line was visible in the gas from radium, and also a bright blue line, absent in the spectrum of the pure dioxide. The spectrum of helium was then thrown in

through a comparison prism, when no doubt remained that the yellow line was actually D^3 . By cooling the U-tube, the emanation and dioxide were condensed, and the helium spectrum increased greatly in brilliancy. After half an hour the tube was sealed off. The position of the D^3 line was confirmed to within one-tenth of the distance between the two sodium lines, D^1 and D^2 .

Experiment 2.—A second apparatus similar to the last was made of entirely fresh glass, so as to exclude any possibility of contamination with helium; and the observation was repeated with 31.8 milligrammes of radium bromide, kindly lent by Professor Rutherford, which had been kept in the solid state at least 3 months. The apparatus was slightly modified, as shown in the dotted lines in fig. 2, so as to avoid taking the gas through the pump. As before, the whole apparatus was washed out with oxygen, and the copper spiral was glowed in oxygen, so as to oxidise it superficially, and so render it able to deal with the excess of hydrogen, as well as with the constituents of the water which had been decomposed. After the gas had been admitted by opening the stop-cocks G and H, the copper spiral was kept glowing for three-quarters of an hour. The U-tube was then cooled with liquid air, and tap D was opened. D^3 was seen. Mercury was admitted to the tubes D and C, and the vacuum-tube was sealed off. It now showed all the visible helium spectrum except the faint least refrangible red, as well as the yellows, green, and violet of mercury. Two unidentified lines were also measured, of approximate wave-length 6145 and 5675, the former faint but distinct, the latter moderately bright. The vacuum tube did not glow visibly in the dark, showing that the emanation had been almost completely removed. The U-tube was next placed in communication with the pump, still surrounded with liquid air, but no gas could be extracted; now the U-tube had probably two or three times the capacity of the vacuum tube; and at the low temperature of liquid air, almost twenty times the quantity of helium must have remained in it. It shone brilliantly in the dark. The passage to the pump was then closed, and the liquid air removed. On again establishing communication, a brilliant phenomenon was observed in the dark; the glowing emanation passed through the capillary somewhat slowly, rushed along the wider connecting tubing was delayed in passing through the tightly packed phosphorus pentoxide, and finally filled the barrel of the Töpler pump. On raising the reservoir, the gas grew more luminous as its volume was

FIG. 3.

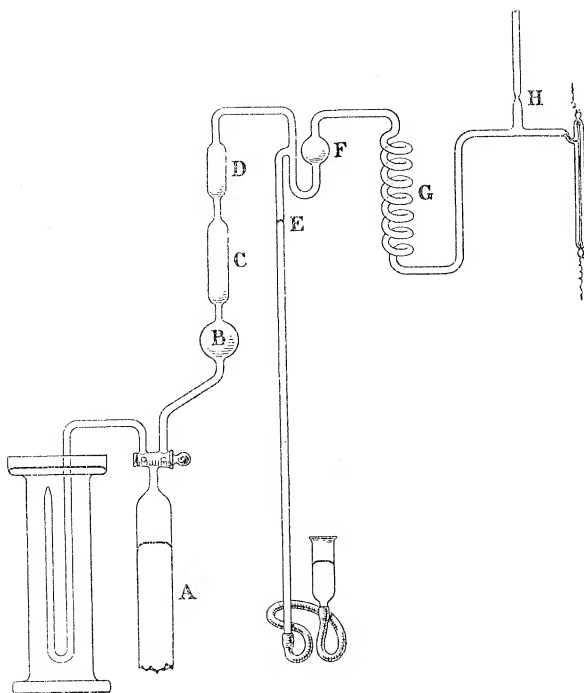


decreased, and on lowering it, the glowing gas appeared to lie on the surface of the mercury for a fraction of a second, falling with the falling mercury; but it soon spread through the whole barrel by diffusion.

The bubble of gas pumped out was treated with a drop of caustic potash, when a considerable fraction was absorbed. By next day the volume of the bubble had increased.

Inasmuch as all samples of emanation showed the spectrum of

FIG. 4.



carbon-dioxide, the presence of which was believed to be due to the oxidation of the tap-grease, an apparatus was constructed in which the use of taps was, as much as possible, avoided. All the emanation from about 60 milligrammes of radium bromide was introduced into the burette A, the only gas present being oxygen. From the burette it passed through the bulb B, which contained concentrated potash solution; it then passed through C, which was charged with solid potash and was deprived of moisture by contact with phosphorus pentoxide in D. The level of the mercury in the trap was at E, so that the emanation reached the spiral G, cooled with liquid air; the

whole of the emanation was washed into the spiral by admission of a little pure oxygen from A ; on exhaustion with the pump the gas was not luminous, showing that the emanation had been almost completely retained in the spiral. Mercury was then allowed to rise in the trap until the bulb F was filled ; the connection to the pump was then sealed at H and the spiral allowed to warm up. The emanation in the vacuum tube showed a bright green spectrum, but on filling the spiral with mercury and sealing off the vacuum tube, the spectrum of carbon dioxide became visible ; D^3 was not seen.

Next day this line was seen, but very feeble ; its strength increased from day to day, and in 5 days the yellow, green, and two blues were visible as well as the violet ; their identity was proved by means of a comparison spectrum.

Subsequent experiments were made in which the heated spiral of copper was replaced by a tube containing a fragment of phosphorus ; the emanation was washed out of the condensing tube by a few bubbles of oxygen. The bulb of potash solution was retained, but the solid potash was replaced by solid barium hydroxide. This plan was not so effective in removing carbon dioxide, yet on keeping the tube for 3 days, and condensing the carbon dioxide with liquid air, D^3 was easily visible, although weakened by the spectrum of carbon monoxide.

On two subsequent occasions the gases evolved from both solutions of radium bromide were mixed after 4 days' accumulation, which amounted to about 2.5 c.c. in each case, and were examined in a similar way. In this case the non-condensable gases alone were examined, the emanation being retained. Whereas with the emanation almost the whole can be introduced into the vacuum tube, with permanent gases only about one-twentieth part is available for the purpose of the spectrum. The D^3 line of helium could not be detected.

The vacation now intervened, and the bulbs containing the dissolved radium bromide were connected with a mercury reservoir and with a gauge, so that the pressure should not rise and burst the bulbs. The gas accumulated during 60 days ; its composition was : Hydrogen, 19.48 c.c. ; oxygen, 10.37 c.c. ; nitrogen 1.02 c.c. = 30.87 c.c.

The nitrogen was manifestly derived from leakage ; after deducting one-fourth of its volume of oxygen, the remaining gas has practically the composition of electrolytic gas. The rate of accumulation is about $\frac{1}{2}$ c.c. a day.

The object of the experiment, of which an account will now be given, was to form an estimate of the amount of helium produced by comparing the intensity of its spectrum with that of a known quantity of helium at a known pressure.

Experiment 3.—This gas was exploded and left a residue of nitrogen

it was then mixed with a large excess of oxygen, and sparked in presence of caustic soda for some hours to remove nitrogen. The oxygen was next withdrawn by means of phosphorus, and the minute bubble left was mixed with a bubble of oxygen, in order to wash it into the apparatus to which the vacuum tube was sealed. As already described, this apparatus did not differ from that shown in fig. 2, except for the fact that the tube containing the copper spiral was replaced by one containing a fragment of phosphorus, in order to withdraw the oxygen. The phosphorus was warmed and withdrew the oxygen. The gas was then forced by means of mercury through a cooled U-tube, and a portion reached the vacuum tube. On passing a current for an instant, the D^3 line was plainly seen, but nitrogen was also present in small amount. The tube was then sealed off.

The volume of the spectrum tube, including the U-tube, had been previously estimated by filling it twenty times with air and pumping out each time; from this measurement the total volume was found to be 0.310 c.c., and after the U-tube had been sealed off, the same process was repeated with the U-tube and connections, minus the spectrum tube. The volume of the spectrum tube was thus found to be 0.165 c.c.

An exactly similar spectrum tube made of the same glass and having the same length was attached to a bulb tube, from which it could be cut off by turning a stop-cock; the bulb tube in its turn could be cut off from the pump by a stop-cock. The capacity of the spectrum tube as well as of the bulb tube was known. A known amount of helium was introduced into the bulb tube and the spectrum tube by means of an inverted syphon furnished with two stop-cocks; the volume between the stop-cocks was 0.0268 c.c. As the volume of the spectrum tube and connections was 1.68 c.c., and that of the bulb was 1.25 c.c., when the gas contained in the spectrum tube was allowed to expand into the evacuated bulb tube, its volume was reduced in the ratio $1.68/1.25 + 1.68$, or 0.57. The spectrum tube containing the fraction of the helium from 60 days' accumulation was placed in series with that containing helium, so that the same current traversed both, and their spectra were compared as regards luminosity of the D^3 line. It was necessary to divide the contents of the helium tube seven times before the D^3 line could be regarded as of comparable intensity in both spectrum tubes. Multiplying this ratio by the volume of the helium admitted at atmospheric pressure into the apparatus, the volume remaining in the apparatus after rarefaction is given:

$$(0.57)^7 \times 0.0268 = 0.000517 \text{ c.c.}$$

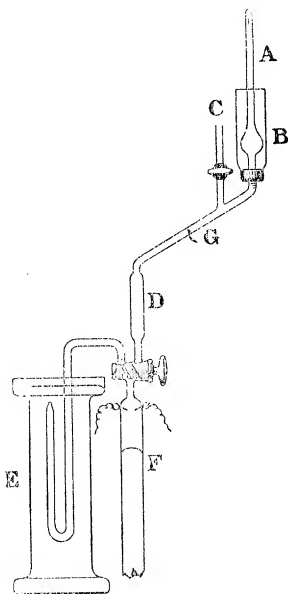
Now, the volume of the helium tube and connections was by chance practically ten times that of the spectrum tube alone (1.65 and 0.165),

hence the spectrum tube contained 0.000052 c.c., or 0.052 cub. mm. The total quantity obtained was twice this amount, or 0.1 cub. mm.

As 1 litre of helium weighs 0.18 gramme, for its density is twice that of hydrogen, 0.1 cub. mm. weighs 0.000018 milligramme. This amount is the product of 50 milligrammes of radium bromide in 60 days; hence, 1 gramme of the bromide should give in a year 0.0022 milligramme. It should be mentioned that the spectrum of argon was present, and it may have seriously interfered with this estimation. The helium, too, may have penetrated and been retained in the glass.

Experiment 4.—It appeared feasible to attempt to measure the actual volume of the emanation in a fine capillary tube. Thinking that any bought capillary tube would be too wide, we drew a very narrow one, which had an electrode sealed into its end. It turned out, however, to be very irregular, and the results as regards volume are not very trustworthy. A is the capillary tube, with a platinum electrode of very fine wire sealed into its upper end; the mixed hydrogen and oxygen containing the emanation were introduced into the explosion burette F through the inverted syphon E; some moist caustic potash had been melted in the top of the burette, so as to remove from the gases any possible carbon dioxide which might have been produced by the flame causing an organic dust in the burette to burn. After the gases had been exploded, the excess of hydrogen, together with the emanation, was allowed to stand for some time in contact with the caustic potash. The upper part of the apparatus having been completely evacuated, the connection with the pump was closed, and the tube leading to the reservoir of the burette was clipped; on making communication by turning the tap of the burette, the hydrogen and the emanation entered the apparatus. Liquid air was then poured into the tube C, so as to cool the bulb B, where the emanation condensed. After raising and lowering the reservoir of the burette several times, in order to convey the emanation into the bulb B, the tap of the burette was closed, and that leading to the pump opened. Again opening cautiously the tap of the burette, the mercury was allowed to rise, passing through the tube D containing phosphorus pentoxide as far as G; the evacuation

FIG. 5.



was then completed until not a trace of a bubble passed through the pump. The tap leading to the pump was closed, and that of the burette opened, until the mercury had risen to near the bulb B. On darkening the room the bulb B was brilliantly luminous; indeed, it was possible to read a watch by its light. The liquid air was allowed to evaporate away, and the reservoir of the burette lowered and its tap opened; by gently raising the reservoir the emanation was all collected in the capillary tube A. The volume of the emanation was read from day to day by help of a reading telescope. It contracted regularly; the tube was coloured deep purple after some days, and this made reading difficult, but by a brilliant illumination behind the rise of the mercury could be followed. No attempt was made to pass a discharge for 28 days; after that lapse of time the emanation had contracted to a volume occupying only 0.1 of a millimetre of the capillary tube at a pressure of about 50 mm., yet it maintained its brilliancy till the very last; only the length of tube illuminated grew shorter and shorter. On freezing out the mercury vapour by cooling the bulb B with liquid air, the helium spectrum was visible, and at the same time the effect of passing the discharge was to reproduce gas in the capillary tube.

After the conclusion of the experiment, the tip of the tube was cut off immediately below the platinum wire, and the capillary depression was measured at different levels. The capillary tube was then cut off, and the volume determined by weighing with mercury; it was then calibrated by a shifting thread of mercury, under a reading microscope. The final results were:—

Time.	Volume.	Time.	Volume.
Start	0.124 cub. mm.	7 days	0.0050 cub. mm.
1 day	0.027 "	9 "	0.0041 "
3 days	0.011 "	11 "	0.0020 "
4 "	0.0095 "	12 "	0.0011 "
6 "	0.0063 "	4 weeks ...	0.0004 "

The comparatively large volume at the start is very remarkable; we can only record it, it may possibly have been due to the mercury sticking in the capillary tube, which was narrower below.

Experiment 5.—The former experiment was repeated, this time with a regular capillary tube, of which the volume per centimetre was 0.24 cub. mm. It was regular in bore, and the depression due to capillarity was 56.2 mm. of mercury. It was heated, as well as the bulb in which the emanation was to be condensed, to incipient redness during evacuation. The emanation was introduced, the accompanying hydrogen pumped off, and the liquid air jacket removed. The volume of the emanation was read at once, at different pressures. The following table gives the lengths of the capillary tube, the corresponding

volumes, the pressures corrected for capillarity, and the products of volume into pressure :—

Length of tube.	Volume in cub. mm.	Pressure in mm.	Volume \times pressure.
6.80	0.163	132.4	21.6
2.30	0.0552	333.4	18.4
1.55	0.0372	518.1	19.3
1.20	0.0288	644.8	18.6
0.95	0.0228	765.8	17.5
2.55	0.0612	309.2	18.9
11.90	0.372	55.3	20.6

The mean value of the product is 19.3, and the volume at normal pressure 0.0254 c.mm. The same afternoon, numerous readings were taken, and it was found that the sticking of the mercury in the capillary tube made it difficult to ascertain the true volume. As the pressure, however, was first raised, and then lowered, the mean cannot be far from the truth. Now, a most remarkable circumstance must be chronicled. Whereas the emanation in the previous experiment contracted during its whole life, in this experiment a regular expansion was observed, rapid at first, and slowly falling off from day to day. Between 5 minutes past 1 o'clock and 7 o'clock, the pressure being kept constant at 55.3 mm., the value of P.V. increased from 20.6 to 48.4. This was on January 20th. On the 21st, the P.V. had increased to 71.2, and remained fairly constant all day, and three small bubbles appeared in the thread of mercury, below the level of the emanation. On the 22nd, the value of P.V. had diminished to 56.5, and the volume of the bubbles had increased to 2.7 mm. length in the tube. On the 23rd, the emanation occupied practically the same volume, but the length of the bubbles had increased to 4.1 mm. The presence of these bubbles made it impossible to obtain correct readings, for the "sticktion" of the mercury was much increased. On the 25th, P.V. had further diminished to 51.2 and the length occupied by bubbles had increased to 5.5 mm. On February 3rd, the bubbles were united with the emanation; the value of P.V. was 132.5 and the volume of the gas under normal pressure, 0.174 cub. mm. On the 9th, the P.V. had increased to 166, and the volume at normal pressure to 0.224 cub. mm. Lastly, the volume of the gas was measured on the 12th at atmospheric pressure; it amounted to 0.262 cub. mm. The level of the mercury was then lowered, and the gas pumped out, it showed a brilliant spectrum of helium. The tube was then heated, and the volume of the absorbed gas was 0.103 cub. mm. at atmospheric pressure; it, too, showed the helium spectrum, but the tube punctured before this could be confirmed.

These results are somewhat inexplicable in the light of the former

experiment. More stringent precautions had been taken to free the capillary tube from gas in the second experiment than in the first, and yet bubbles appeared below the surface of the mercury. It may be that owing to the quality of the glass of which the first tube was made, the helium found means to enter into its substance more easily than into that of the second. But at any rate, the volume produced is of the same order, as the following considerations will show.

On the view that the emanation results from a definite fraction of the radium disintegrating per second, this fraction can be calculated from the volume of the emanation, and the time of accumulation. The emanation accumulates until the rate of production is balanced by the rate of disappearance, and then the quantity remains constant. Let Q_{∞} be the equilibrium quantity, and Q_t the quantity present after time t ,

$$Q_t/Q_{\infty} = 1 - e^{-\lambda t},$$

where t is expressed in seconds, and λ is a constant representing the proportion of the emanation changing per second, and equals $1/463,000$.* The radium bromide employed weighed about 60 milligrammes. Assuming that the compound contained about half its weight of the element (radium, 225; bromine + $2H_2O$, 196), the quantity of radium may be taken as about 0.03 gramme. In the first experiment, the time of accumulation t was 8 days = 691,200 seconds; Q_t therefore equals $0.775 Q_{\infty}$. The volume taken (0.027 cub. mm.) in the first experiment was that at the end of the first day, and a correction must be applied to allow for the amount that had changed in this interval. The quantity remaining after the lapse of 1 day is 0.83 of the initial quantity. The volume, 0.027 cub. mm., is therefore

$$0.83 \times 0.775 Q_{\infty} = 0.643 Q_{\infty}.$$

The average life of the particle in a system in which a constant fraction λ of the number of particles changes per second can be shown to be $1/\lambda$. The equilibrium quantity, Q_{∞} , is the quantity produced in the period of average life of the atom of the emanation, or $Q_{\infty} = Q_0/\lambda = 463,000 Q_0$, where Q_0 is the quantity produced per second. And $0.643 Q_{\infty} = 297,830 Q_0$. The volume of Q_0 is thus $0.027/297,830 = 0.9 \times 10^{-7}$ cub. mm. This is in the case of 0.03 gramme of radium; 1 gramme of radium, therefore, produces 3×10^{-6} cub. mm. of emanation per second.

Since the emanation resembles the gases of the argon family in chemical inertness, its molecule is probably monatomic, and its atomic weight must be twice its density in terms of hydrogen as unity. The density is not accurately known; but diffusion experiments indicate a value of about 80. The atomic weight being therefore in the neigh-

* Rutherford and Soddy, 'Phil. Mag.,' 1903, 6, vol. 5, pp. 445 and 576.

bourhood of 160, not more than one atom of emanation can be produced from one atom of radium. To determine the ratio between the quantity of emanation and the quantity of radium producing it, it is necessary to know the volume that would be occupied by the radium in the form of monatomic gas. This is for 1 gramme of radium $(2 \times 11.2)/225 = 0.1$ litre $= 10^5$ cub. mm. One gramme of radium produces 3×10^{-6} cub. mm. of emanation per second, and if one atom of radium produces one atom of emanation, then λ , the proportion of the radium changing per second, is 3×10^{-11} . The proportion changing per year is 9.5×10^{-4} ; thus slightly less than one-thousandth part changes per year. The average life of the radium atom is $1/\lambda = 3.3 \times 10^{10}$ seconds $= 1050$ years.

In the second experiment, the emanation was accumulated 6 days, and measured 0.0254 cub. mm. In this case,

$$Q_t = 0.674 Q_{\infty} = 312,060 Q_0,$$

and $Q_0 = 0.81 \times 10^{-7}$ cub. mm.; $\lambda = 2.4 \times 10^{-11}$, and $1/\lambda = 1250$ years. The mean of the two experiments, therefore, gives for 1 gramme of radium (element) $Q_0 = 2.85 \times 10^{-6}$ cub. mm.; $Q_{\infty} = 1.3$ cub. mm., $\lambda = 2.85 \times 10^{-11}$, and $1/\lambda = 1150$ years.

Rutherford and Barnes* have shown that 75 per cent. of the total heat-evolution of radium which has reached its equilibrium state is derived from the emanation and its subsequent products of change. Since 1 gramme of radium evolves 100 calories per hour (Curie), 1.3 cub. mm. of emanation emit 75 calories per hour. The total quantity of heat H emitted during the complete change is given by multiplying h the emission per second, by the average life of the emanation in seconds, thus giving $H = h/\lambda = 9,646$ calories. One c.c. of emanation would therefore emit 7.4×10^6 calories during its complete change. A cubic centimetre of hydrogen and oxygen in the proportion required to form water evolve 2.04 calories on explosion, or a quantity 3,600,000 times less than is emitted by an equal volume of the radium emanation. If the density of the emanation is assumed to be 100, the ratio of the energies emitted by equal weights of emanation and of water is 216,000 to 1.

The total quantity of energy evolved during the change of 1 gramme of radium is given by multiplying the energy emission per second by the average life of the radium atom in seconds, and is 10^9 calories. The energy evolved in the formation of 1 gramme of water is 3.8×10^3 calories; hence the ratio is again about 250,000 to 1.

The volume of Q_{∞} , the equilibrium quantity of emanation produced by 1 gramme of radium, was theoretically calculated by Rutherford† from the energy emitted by radium per second, and the energy of

* 'Phil. Mag.,' 1904, 6, vol. 7, p. 202.

† 'Nature,' August 20, 1903.

the α -particle, as calculated from its mass and its velocity. By making certain assumptions about to be considered, he deduced that Q_{∞} must lie between 0.6 and 0.06 cub. mm. The maximum estimate, which is almost exactly one-half the experimental value found by us, was based on the assumption that the whole, and the minimum estimate on the assumption that only one-tenth, of the energy of disintegration is manifested in the kinetic energy of the α -particle expelled. It was further assumed that only one α -particle was expelled from each atom, at each disintegration accompanied by α -radiation that is known to occur. If more than one α -particle is expelled at each disintegration, the theoretical estimate must be correspondingly reduced. Since the experimental value exceeds the maximum theoretical estimate, it follows that there are now direct experimental reasons for believing that—

(1) Only one α -particle is expelled from the atom at each disintegration.

(2) The greater part of the energy of disintegration appears in the form of kinetic energy of α -radiation.

(3) The emanation is a monatomic gas.

It must be remembered that the experimental value is necessarily a maximum value; for if any impurity were present with the emanation, it would increase the volume measured.
